

PROCESS FOR FILLING TEETH

This is a continuation of application Ser. No. 233,951, filed Feb. 17, 1981, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention concerns adhesive formulations and related methods of adhesion involving the use of materials sensitive to radiation. More particularly, this invention relates to adhesives which are adapted to being cured or set on demand by application of radiant energy, especially visible or ultraviolet light. Such adhesives are formulated employing a major proportion of certain silane species. Optionally, these formulations may contain non-silane polymerizable ethylenically unsaturated materials such as acrylic species. According to a preferred embodiment, such adhesives may be used for various adhesive applications in dentistry.

It has been desired to employ as adhesives formulations which are suitable for use in "demand settable" adhesive processes. Such a process would employ adhesives which do not begin to cure or harden until a preselected point in time and then are set in a relatively short period of time after curing is initiated.

It has also been desired to employ certain silane species in adhesive formulations. Such employment of silanes has been thought to lend certain beneficial properties to the adhesives thus constituted. Accordingly, such adhesives are believed to be relatively impervious to water and to coat surfaces to be joined in a desirably uniform manner. For certain adhesive uses, it is desirable to employ adhesives which are not easily degraded by heat. In typical commercial adhesives, the application of high temperatures tends to cause thermal breakdown of the compositions with concomitant loss of physical and chemical properties and liberation of noxious odors. At present, only a limited number of adhesives, such as the zinc and other metal phosphates, and certain epoxy and phenolic resins are well adapted for resistance to thermal degradation; none of these is demand settable.

2. Description of the Prior Art

It has been known to employ certain silanes in polymerizable compositions including radiation polymerizable compositions. Such employment has usually been for the purpose of securing good bonding of resin matrices with fillers or with substrates. Silanes have also been employed for viscosity modification of resin systems. The usual mode of polymerization of silanes in polymerizable resins is thermal; radical inhibitors are frequently included to prevent premature thermal polymerization. It has not been known to employ silanes as principal constituents of actinic light polymerization compositions; it has generally been thought that photopolymerization of such resins would proceed sluggishly. Use of silanes as polymerizable constituents of demand set adhesives has been, accordingly, unknown.

OBJECTS OF THE INVENTION

It is an object of this invention to provide adhesive formulations which are demand settable. It is another object to provide such adhesives which comprise silane species in major proportion. Yet another object is to furnish adhesives which are capable of withstanding elevated temperatures without substantial degradation, loss of physical properties and liberation of noxious

odors. It is also desired that the adhesives of this invention be relatively impervious to water and to demonstrate good coating of substrates. Another object is to provide such compositions which are suitable for industrial assembly processes such as fixturing. A further object is to provide adhesion processes employing such materials. A particular object is to develop such processes which are adaptable for use in dentistry. These and other objects are accomplished through the employment of one or more embodiments of the present invention.

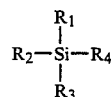
SUMMARY OF THE INVENTION

It has been discovered that demand settable adhesives may be formulated employing certain silane species together with a photosensitizing system. Such adhesives may be set on demand by the application of suitable actinic light radiation. Such adhesives are water resistant, exhibit good substrate coverage, and show improved resistance to degradation at elevated temperatures. These adhesives comprise a polymerizable resin comprising at least about 20% by weight of at least one light polymerizable silane. Other ethylenically unsaturated polymerizable species may also be included such as acrylates, methacrylates, and vinyl compounds. The adhesives may, optionally, be filled. The photosensitizing system may preferably comprise an alpha diketone and an amine. Depending upon the radiation sensitizing system thus chosen, these adhesive formulations will polymerize when they are exposed to the appropriate radiation, such as visible light. In certain embodiments, it has been found desirable to supplement the photosensitizing system with a peroxide or other polymerization promoting species to facilitate the rapid polymerization and setting of the adhesives.

DETAILED DESCRIPTION OF THE INVENTION

The adhesive compositions of this invention comprise polymerizable resins comprising at least 20% by weight of certain polymerizable silane and related species, up to 80% by weight of a polymerizable ethylenically unsaturated material and an amount of a photosensitizing system effective to cause polymerization of the adhesive when it is exposed to actinic light. Such adhesives may also comprise organic or inorganic fillers and other modificants.

The silanes which are suitable for use in the practice of this invention are any of those silanes which contain functionalities which participate in photochemical polymerization. In general, such silanes have one or more reactive ethylenic unsaturations. Such unsaturations include, for example, vinyl, allyl, "dienyl", acetylenyl, acrylyl, methacrylyl, other acrylic homologs, and many other reactive ethylenic functionalities. Preferably, such silanes belong to the class of acrylosilanes, which class includes methacrylic and homologous species. Such families may be represented by the formula:



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where R_1 - R_4 are the same or different and may be H, alkyl, alkenyl, aryl, aralkyl, alkaryl, alkoxy, vinyl, aryl-oxy, acyloxy etc. having from 1 to about 30 carbon